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SOME NEW N-BENZOYL-N'-SUBSTITUTED PHENYL THIOUREA COMPLEXES OF COPPER(II)

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ABSTRACT

The new N-benzoyl-N'-substituted phenyl thiourea ligands have been used to prepare copper(II) complexes [$Cu(L)_2Cl_2$]. The novel complexes were characterized by ESR, IR, NIR, electronic spectroscopy and conductivity measurements. Tentative geometry of the complexes involves four-coordinate environments (tetrahedral distorted D_{2d}) for the copper ion and a monodentate behaviour for ligands. In all these complexes N,N'-substituted thiourea is sulphur-bonded to the copper ion.

RESUMO

Os novos ligantes de N-benzoila-N'-substituidos por feniltiourea foram usados para preparar complexos os complexos $Cu(L)_2Cl_2$. Os novos complexos foram caracterizados usandos métodos de RSE, infravermenlo, infra-vermelho próximo,espectroscopia eletrônica e medidas de condutividade. A geometria proposta tentativamente para os complexos envolve ambientes tetra-coordenados (D_{2d},tetraédrico distorcido) para o íon de cobre e comportamento monodentado para os ligantes. Em todos os complexos a N,N'-tiouréia sunstituida está ligada ao íon de cobre através do átomo de enxofre.

KEYWORDS : thiourea, copper(II), complexes, ESR spectra.

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INTRODUCTION

A numerous series of thiourea and some N or N,N'-substituted thioureas complex with transition metals are reported in literature[1-4], and the N-benzoyl-N'-substituted thiocarbamides have received very little attention[5,6]. These compounds are used succesufully as extractive reagents[7,8]. The coordination behaviour of these derivatives of thiourea is very interesting due to three donor sites for the coordination: the sulfur atom of the C=S group, the oxygen atom of the C=O group and the nitrogen atoms of the NHR groups. We therefore prepared some new N-benzoyl-N'-phenyl substituted thioureas complexes with copper(II) in order to study the coordination and stereochemistry via the synthesis ways.
The structure of the formed Cu(II) complexes was established via phisicochemical studies including IR, NIR, UV-VIS, ESR spectral and conductance measurements.

EXPERIMENTAL PART

Reagents of the best chemical grade were used.

The ligands N-benzoyl-N'-phenyl substituted thioureas were prepared according to the procedure described elsewhere[9]. The copper(II) complexes of the ligands L_1 -L_7 (fig. 1), may be prepared by addition of an methanolic solution containing 2mM of copper(II) chloride to an methanolic suspension containing 4mM of the ligand. In each case the copper(II) complex is formed as a yellow-orange solid. The complexes are stable under atmospheric conditions and are soluble in chloroform, DMF and partially in acetone. If an aqueous solution of the sodium salt of the L_1 ligand was added to an aqueous solution of copper(II) chloride a $[CuL_1H_2O]$ complex type[10] is formed.

Phisical measurements

Elemental analysis were been performed with a Carlo Erba L1108 model automatic analyzer (C, N), with AAS-1N Carl Zeiss Jena spectrometer (Cu) and Mettler Toledo 355 Ion Analyzer (Cl). The electronic spectra of all compounds were obtained, in solution (chloroform), with a SHIMADZU UV 160A spectrophotometer. The IR spectra were run with a FT-IR BIO RAD FTS spectrophotometer in the 4000-500 cm^{-1} and with a SPECORD M80 Carl Zeeiss Jena spectrophotometer in the 500-250 cm^{-1}, in KBr pellets and NIR spectra with NIR Systems spectrophotometer.. The ESR spectra of copper(II) complexes were measured on polycrystalline powders with VARIAN E-9. Conductivities were measured at room temperature in dimethylformamide (DMF) with a HACH TDS-meter.

RESULTS AND DISCUSSION

Colours, analytical data and conductivity values for the complexes are given in Table 1. As outlined by the analytical data in Table 1, the composition of the compounds may be represented as $[Cu(L)_2Cl_2]$. The molar conductivities in DMF shows that these complexes are non-electrolytes.

The structure of the ligands can be represented in a variety of ways, two containing the tioketo group(I, II) and the other two in the thiol forms (III, IV) (fig. 1).

Table 1. Analytical data, colours and molar conductivity for the [Cu(L)$_2$Cl$_2$]complexes.

Compound	Colour	Analysis%								Λ_M
		C		N		Cl		Cu		
		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	
[Cu(L$_1$)$_2$Cl$_2$]	yellow pale	53.94	54.66	7.20	7.97	9.80	10.08	8.84	9.04	39.5
[Cu(L$_2$)$_2$Cl$_2$]	yellow	53.29	54.66	7.35	7.97	9.70	10.08	8.87	9.04	44.8
[Cu(L$_3$)$_2$Cl$_2$]	yellow canar	53.90	54.66	7.13	7.97	9.15	10.08	8.90	9.04	43.3
[Cu(L$_4$)$_2$Cl$_2$]	yellow canar	53.85	54.66	7.17	7.97	9.72	10.08	8.78	9.04	42.4
[Cu(L$_5$)$_2$Cl$_2$]	yellow cream	55.22	55.85	6.98	7.66	9.53	9.70	8.20	8.69	28.9
[Cu(L$_6$)$_2$Cl$_2$]	orange	44.80	45.20	9.91	10.54	8.20	8.90	7.53	7.97	43.3
[Cu(L$_7$)$_2$Cl$_2$]	yellow pale	50.12	50.96	7.05	7.92	9.32	10.03	8.75	8.99	26.0

*The conductivity values is given in ohm^{-1}·cm^2·mol^{-1}.

Table 2. IR bands (cm^{-1}) of N-benzoyl-N'-substituted phenyl thioureas.

Compound	ν(C=O)	ν_{asym}(N-C-N)	ν_{sym}(N-C-N)	ν(C-S)	ν(C-NO$_2$)	ν(C-O-CH$_3$)
L$_1$	1670	1530,1506	1330	731	-	-
L$_2$	1670	1531,1523	1335	730	-	-
L$_3$	1668	1553,1528	1350	725	-	-
L$_4$	1670	1561,1528	1350	710	-	-
L$_5$	1668	1527,1504	1330	720	-	-
L$_6$	1672	1523, -	1314	720	1345	1268
L$_7$	1668	1536,1510	1340	736	-	1270

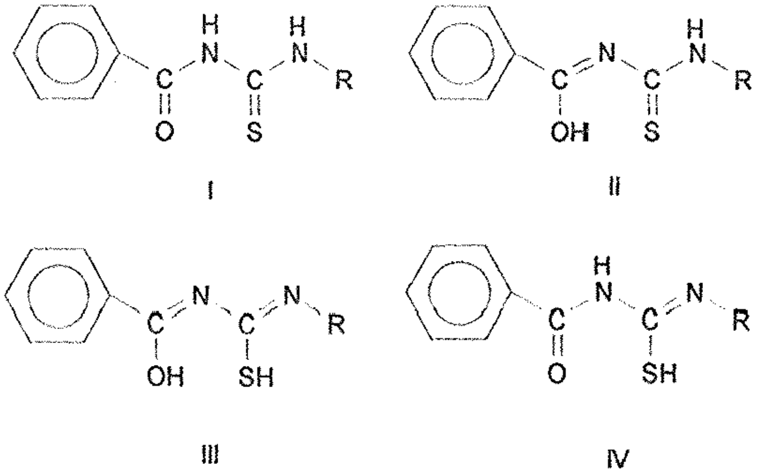
Table 3. IR bands (cm^{-1}) of N-benzoyl-N'-substituted phenyl thioureas copper(II) complexes.

Compound	ν(C=O)	ν_{asym}(N-C-N)	ν_{sym}(N-C-N)	ν(C-S)	ν(C-NO$_2$)	ν(C-O-CH$_3$)
[Cu(L$_1$)$_2$Cl$_2$]	1670	1533	1330	685	-	-
[Cu(L$_2$)$_2$Cl$_2$]	1674	1534	1333	685	-	-
[Cu(L$_3$)$_2$Cl$_2$]	1671	1553	1322	685	-	-
[Cu(L$_4$)$_2$Cl$_2$]	1670	1528	1320	668	-	-
[Cu(L$_5$)$_2$Cl$_2$]	1666	1533	1323	686	-	-
[Cu(L$_6$)$_2$Cl$_2$]	1681	1525	1306	684	1353	1276
[Cu(L$_7$)$_2$Cl$_2$]	1670	1513	1353	680	-	1270

Table 4. Electronic spectra (recorded in chloroform) of L$_1$-L$_7$ ligands and their copper(II) complexes(cm^{-1}).

	Ligands	Complexes	
L$_1$	39200, 36650	[Cu(L$_1$)$_2$Cl$_2$]	39400, 33000, 7680
L$_2$	39850, 37300	[Cu(L$_2$)$_2$Cl$_2$]	39200, 37000, 6800
L$_3$	39200, 36300	[Cu(L$_3$)$_2$Cl$_2$]	39500, 31250, 8050
L$_4$	39500, 36300	[Cu(L$_4$)$_2$Cl$_2$]	39100, 32250, 8010
L$_5$	39700, 35850	[Cu(L$_5$)$_2$Cl$_2$]	38600, 35700, 7300
L$_6$	37600, 27000	[Cu(L$_6$)$_2$Cl$_2$]	38800, 27000, 7520
L$_7$	39500, 36500	[Cu(L$_7$)$_2$Cl$_2$]	39200, 35700, 7280

Fig. 1.



where R = 2,3-dimethylphenyl (L_1)
3,4-dimethyphenyl (L_2)
2,4-dimethylphenyl (L_3)
2,5-dimethylphenyl (L_4)
2-ethyl-6-methylphenyl (**L_5**)
2-nitro-4-methoxyphenyl (L_6)
4-methoxyphenyl (L_7)

Fig. 1. Structure of the Ligands Used.

The main IR bands of the ligands L_1-L_7 and their copper complexes are listed in Tables 2 and 3.

The IR spectra of the ligands is highly complex and shows a larger number of bands. We have not attempted to make a complete analysis of the spectra; however attention has been focused on a limited number of bands which provide considerable structural significance in order to suggest the most probable manner of coordination of the ligand with copper(II) ion. It has been stated the thione group (C=S) is relatively unstable in the monomeric form and tends to a stable C-S single bond by enethiolization, if there is at least one hydrogen atom adjacent to the C=S bond. The IR spectra of L_1-L_7 do not display any vibrational (S-H) bond near 2500 cm^{-1} indicating that, at least, in the solid state they remain in the thione form. The carbonyl stretching band appears ~1670 cm^{-1}. The position of this band is not changed in the IR spectra of the complexes suggesting that C=O group is not involving in coordination to the copper ion. The characteristic absorption region of (C=S) stretching are reported in the free thiocarbamide at 730, 1080, 1120 and 1400 cm^{-1}. A relatively sharp band of medium intensity appears in the spectra of ligands at 710-730 cm^{-1} which most probably arises due to C=S stretching vibrations. In the metal complexes this band disappears and another band of same intensity appears in the range 670-685 cm^{-1}. This observation indicates the shift of ligand ν(C-S) vibration towards a lower frequency region and further attribute the coordination of C=S group with the copper(II) ion.

In the region 1500-1560 cm^{-1} there are two strong bands. These twin bands can be attributed to ν_{asym}(N-C-N) stretching vibrations. In all the complexes spectra one of these twin bands disappears suggesting also the participation of C=S group in coordination. In the far infrared, several new bands are observed in the spectra of the complexes, typical of the M-S (300-320 cm^{-1}) vibrations[11,12].

The electronic spectroscopy data for ligands and their copper complexes, in solution (chloroform), are quoted in Table 4.

Table 4

All these derivatives of thiourea have a strong band due to a n→ π* transition at ca 39500 cm^{-1} and a second π→ π* at ca 36500 cm^{-1} (except for L_6 at 27000 cm^{-1}). Both of these are found in the electronic spectra of complexes. All the electronic spectra of copper(II) complexes exhibits an absorbtion in the 7000-8000 cm^{-1} region which it may be assigned to a $^2B_2 \rightarrow {}^2E$ transition[13], comparable to those reported for four-coordinate complexes, distorted tetrahedral environment (D_{2d}).

Figures 2,3

The ESR spectrum obtained on polycrystalline powder at room temperature of $[Cu(L_1)_2Cl_2]$ is shown in Fig. 2. For the $[CuL_1H_2O]$ complex the ESR spectrum is shown in Fig. 3. The ESR spectrum of $[Cu(L_1)_2Cl_2]$ complex quite different from those of the $[CuL_1H_2O]$ which posses an octahedral tetragonal distorted geometry[10,14], this compound being prepared in different conditions (alcaline medium).

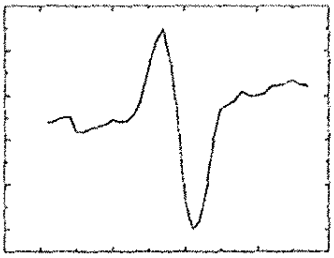


Fig. 2. The ESR spectrum of $[Cu(L_1)_2Cl_2]$ complex (g = 2.2228, ΔH=111.25G)

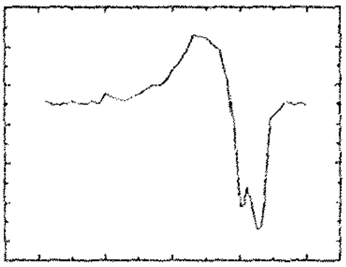


Fig. 3. The ESR spectrum of the $[CuL_1H_2O]$ complex ($g_{\parallel}$=1.9667, $g_{\perp}$=2.1410 and ΔH=111G)

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